

Electrocatalytic Properties of Composite Conducting Polymer and Metal Oxide Based Films Towards Methanol Oxidation and Oxygen Reduction

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There is a need to produce highly functionalized, hybrid, conducting polymer and metal oxide based electrocatalytic films of controlled architecture and thickness as well as to develop methods for their micro- and nanopatterning. In the present work, we propose and develop the concept based on multiple formation of two-dimensional layers composed alternately of conducting polymers (such as polyaniline or polypyrrole) and polynuclear inorganic compounds (such as metal oxide or polyoxometallate of molybdenum and tungsten). In the procedure, a ca. monolayer of the inorganic heteropolyanion is first adsorbed onto the electrode surface. By immersing the resulting self-assembled monolayer into a solution of organic monomer, a composite (hybrid) layer is formed due to the interaction between the adsorbed (inorganic) polyanion and the solution cationic (organic) species. The actual polymerization step can be controlled both chemically, by choosing a polyoxometallate with sufficiently oxidative potential, or electrochemically by applying sufficiently positive potential to the system upon medium transfer to electrolyte. Details of the preparation and physicochemical, particularly electrochemical, properties of the produced films will be described. By repeated and alternated immersions (treatments) in the appropriate solution, the amount of material on the electrode surface can be increased systematically in a controlled fashion leading to stable three-dimensional multilayered assemblies. Consequently, the thickness, composition, and physicochemical properties of the resulting coatings can be varied and tailored to practical needs. Our results also indicate that the incorporation of a polymeric backbone within the inorganic monolayer units significantly increase the stability of films.

Our goal is to fabricate electrocatalytic modified electrodes in which reactive centers are three-dimensionally distributed within thin films attached to electrode substrates. In principle, the resulting systems can possess both the experimental advantage of heterogeneous catalysts and the reactivity or selectivity of the homogeneous analogs. For methanol oxidation, the optimum electrocatalytic film would utilize Pt nano or microcenters codispersed with Ru species in a suitable matrix. In addition to "conventional" metallic ruthenium, we consider polynuclear oxocyanoruthenium microstructures which can be viewed as mixed-valence ruthenium oxo species crosslinked with cyanoruthenates. As a means for immobilization of platinum and ruthenium reactive centers, we propose tungsten oxides, conducting polymers (polypyrroles, polyaniline), self-assembled structured multilayered films composed of alternate

conducting polymer and polyoxometallate "two-dimensional" layers.

To facilitate electroreduction of oxygen, we have produced bifunctional assemblies containing two reactive species, dispersed platinum catalytic centers and tungsten oxide or self assembled conducting polymer-heteropolytungstate matrix. In the course of dioxygen reduction, tungsten(VI,V) oxo species show themselves catalytic reactivity towards electroreduction of the hydrogen peroxide intermediate (generated at small Pt loadings). Generation of W(VI,V) mixed-valence centers also facilitates conduction of electrons to Pt sites. From the mechanistic point of view, the catalytic process is presumably initiated at traces of Pt (reduction of oxygen to hydrogen peroxide), and it is continued at hydrogen tungsten oxide bronzes or heteropolyblues. The possibility of the existence of synergistic effects between platinum particles and tungstate support should be mentioned. We show that immobilization of traces of platinum in tungsten oxide or in hybrid heteropolytungstate-conducting polymer coatings produces bifunctional microstructures which utilize effectively low loadings of precious platinum in the catalytic electroreduction of oxygen. Introduction of conducting polymer (polypyrroles, polyaniline) has a stabilization effect and further enhances the system's reactivity towards oxygen reduction.